THE VARIATION OF THE REST EFFECT WITH THE LIGAND IN SELECTED Cu(II), Zn(II), Cd(II) and Fe(II) COMPLEX SYSTEMS

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Robert Williamson

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I. Introduction

The characteristic behavior of the transition group metal ions to combine with a definite number of molecules of a Lewis base (electron pair donor) when both the metal and the Lewis base are present in solution is well known (9), (13), (15), (16), (17) and (33). A typical example of this type of chemical behavior can be illustrated with the Co^{+2}-NH_3 system. In the Co^{+2}-NH_3 system, the Co^{+2} ion has the capacity of combining with from one to six ammonia molecules. The maximum number of molecules of Lewis base used is a characteristic of the metal ion and is called the maximum coordination number, N.*

With Basolo and Murmann (5), Baxendale and George (8), Bjerrum (9), (10), (11), and Kolthoff, Leussing and Lee (25), (26), it is postulated that the formation of complex ions in aqueous solution is always stepwise and that the stability of the separate species existing in solution is characterized by a series of equilibrium mass action constants hereafter called consecutive complexity constants.

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* Coordination number is usually designated C.N. The use of N to denote maximum coordination number is dictated somewhat by its repeated use in mathematical formulas. On the other hand n is used to indicate the number of molecules of Lewis base coordinated with the metal ion in a coordination complex. See Appendix I, Symbols.

For example, again considering the Co^{+2}-NH_3 system, the consecutive complexity constants are designated k_1, k_2, k_3, ... k_6 and the following equations may be written:

$$Co^{+2} + 6NH_3 \overset{k_1}{\rightleftharpoons} [Co(NH_3)]^{+2} + 5NH_3 \overset{k_2}{\rightleftharpoons} [Co(NH_3)_2]^{+2} + 4NH_3$$
$$\overset{k_3}{\rightleftharpoons} [Co(NH_3)_3]^{+2} + 3NH_3 \overset{k_4}{\rightleftharpoons} [Co(NH_3)_4]^{+2} + 2NH_3$$
$$\overset{k_5}{\rightleftharpoons} [Co(NH_3)_5]^{+2} + NH_3 \overset{k_6}{\rightleftharpoons} [Co(NH_3)_6]^{+2}$$

where the consecutive complexity constants k_1, k_2 and k_n are

$$k_1 = \frac{[Co(NH_3)]^{+2}}{[Co^{+2}][NH_3]} \qquad k_2 = \frac{[Co(NH_3)_2]^{+2}}{[Co(NH_3)]^{+2}[NH_3]}$$

$$k_n = \frac{[Co(NH_3)_n]^{+2}}{[Co(NH_3)_{n-1}]^{+2}[NH_3]}$$

For the general case where metal M is coordinating N molecules of Lewis base, hereafter called the ligand A:

$$M^{+x} + NA \overset{k_1}{\rightleftharpoons} MA^{+x} + (N-1)A \overset{k_2}{\rightleftharpoons} MA_2^{+x} + (N-2)A \overset{k_3}{\rightleftharpoons} MA_3^{+x} + (N-3)A$$
$$\overset{k_4}{\rightleftharpoons} MA_4^{+x} + (N-4)A \quad ..... \quad \overset{k_N}{\rightleftharpoons} MA_N^{+x}$$

where the general term is $MA_n^{+x} + (N-n)A$

and as before

$$k_1 = \frac{[MA]^{+x}}{[M^{+x}][A]} \qquad k_2 = \frac{[MA_2]^{+x}}{[MA]^{+x}[A]}$$

$$k_n = \frac{[MA_n]^{+x}}{[MA_{n-1}]^{+x}[A]}$$

where M represents the solvated central ion and MA_N the coordinately saturated complex ion. In the preceding expressions for the consecutive complexity constants, concentrations are used in place of activities for the sake of simplicity.

The immediate practical value of a complete knowledge of the consecutive complexity constants is that it enables the investigator to calculate the concentration of each complex species existing in solution when the total concentration of metal ion and of ligand is known.

Bjerrum's contribution to the known techniques for determining the consecutive complexity constants was the introduction and use of the glass electrode to follow the concentration of one component of the system. The glass electrode may be used in ammoniacal solutions of metal salts to measure the pH, provided that the pH is less than 10, the point at which the electrode itself is attacked (9).

More recently a study was conducted at the National Printing Ink Research Institute at Lehigh University by Myers (33) in an effort to systematize knowledge concerning complex oxidation catalysts. The goal of this program was to find either an accelerator or a substitute for conventional printing ink driers. A secondary objective was an explanation of the chemical role of the catalyst in the oxidation of linseed oil, in the expectation that then new driers could be synthesized according to specification. This investigation was successful in finding a theoretical explanation for the observed effects of complex catalysts upon drying of oleoresinous vehicles. A cryoscopic technique was used to test the hypothesis advanced.

This paper is concerned with the quantitative relationships existing between the statistical and rest effects in a complex system. Since numerical relationships exist for the statistical effect, the main effort has been toward a quantitative evaluation of the rest effect. Definition of the statistical and rest effect has been deferred to Section II.

II. Theory

A. Introduction

A discussion of the consecutive complexity constants and the interrelationship between these constants can best be undertaken by using Bjerrum's notation (9) as a starting point. The following terms will be needed in the subsequent discussion:

$$T_{n,n+1} = S_{n,n+1} + L_{n,n+1} \qquad (1)$$

where $T_{n,n+1}$ = Total effect; for example $T_{1,2} = \log \frac{k1}{k2}$
$S_{n,n+1}$ = Statistical effect
$L_{n,n+1}$ = Ligand effect
n = Number of molecules coordinated with the metal ion and $S_{n,n+1}$ represents the joint contribution to the ratio of the consecutive complexity constants assignable to purely statistical causes. $L_{n,n+1}$ represents the joint contribution to the ratio of consecutive complexity constants assignable to the individual characteristics of the ligands taken up. The ligand effect can be considered to be divided into two effects such that

$$L_{n,n+1} = E_{n,n+1} + R_{n,n+1} \qquad (2)$$

where $E_{n,n+1}$ = Electrostatic effect
$R_{n,n+1}$ = Rest effect
and $E_{n,n+1}$ represents the electrostatic contribution which exists if the ligand is electrically charged. It represents the electrical work required to move the ligand A from infinity to MA_{n-1} to produce MA_n. If the ligand is neutral,

the electrostatic effect is not necessarily zero because both ends of a polar molecule are not brought to the same distance from the cation. When dealing with neutral coordinating molecules, as for example NH_3, it will be assumed that the electrostatic effect is zero by definition. Therefore, all deviations from statistical behavior in these systems will be manifest in the rest effect. $R_{n,n+1}$ represents that part of the ratio of consecutive complexity constants which can not be explained either statistically or electrostatically. In systems where $E_{n,n+1} = 0$, $R_{n,n+1}$ necessarily equals $L_{n,n+1}$. Since $T_{n,n+1} = \log \frac{k_n}{k_{n+1}}$, then

$$T_{n,n+1} = \log \frac{k_n}{k_{n+1}} = S_{n,n+1} + R_{n,n+1} \qquad (3)$$

B. The Statistical Effect

If with Adams (1) and Bjerrum (9), it is assumed that the statistical tendency of compound MA_n to split off a ligand is proportional to the number of ligands bound, or n , and its statistical tendency to take up a ligand is proportional to the number of positions remaining in the coordination sphere, or N-n, the following statistical ratios are obtained for the N consecutive complexity constants:

$$\frac{N}{1}, \frac{N-1}{2} \ldots \frac{N-n+1}{n}, \frac{N-n}{n+1} \ldots \frac{2}{N-1}, \frac{1}{N}$$

where N = maximum coordination number
n = number of ligands bound to central metal ion in complex.

Hence, an expression in terms of N and n is obtained for the ratio of the statistically expected consecutive complexity constants

$$\frac{k'_n}{k'_{n+1}} = \frac{(N-n+1)(N-n)}{(N-n)\ n} \qquad (4)$$

providing that other influences such as asymmetry, non-statistical chemical and electric forces, and steric hindrance may be disregarded. In equation (4), $\frac{k'_n}{k'_{n+1}}$ is the ratio of the statistically expected consecutive complexity constants. Then, the statistical effect $S_{n,n+1}$ may be defined as

$$S_{n,n+1} = \log \frac{k'_n}{k'_{n+1}} = \frac{(N-n+1)(N-n)}{(N-n)\ n} \qquad (5)$$

Equation (5) is valid when a) the N coordination positions of the metal ion are uniform, and b) each ligand occupies only one coordination position (9).

Hence, if the statistical effect were the only effect operative, the total effect would equal the statistical, and

$$T_{n,n+1} = S_{n,n+1} = \log \frac{k_n}{k_{n+1}} \qquad (6)$$
$$S_{1,2} = \log \frac{k1}{k_2}$$

None of the systems investigated here have obeyed this relation, nor would they have been expected to follow such a simple pattern of chemical reactivity.

Aqueous solution equilibria can be adequately represented by using N+1 N-pronged models. In order to proceed it must be assumed that there are N+1 or more metal ions

present and $\sum_{x=0}^{x=N}$ N-x or more ligand molecules present. This assumption seems justified even at extremely dilute concentrations.

After setting up the model, it is desired to ascertain the statistical ratio of the complexity constants. The answer is obtained by dividing the number representing the tendency to form species n by the number representing the tendency to destroy species n. From Figure 1

$$\frac{k_3^1}{k_4^1} = \frac{2/4 \times 4/4}{1/4 \times 3/4} = 8/3$$

which results from a treatment based on species 3. Comparison with equation (4) shows the same result:

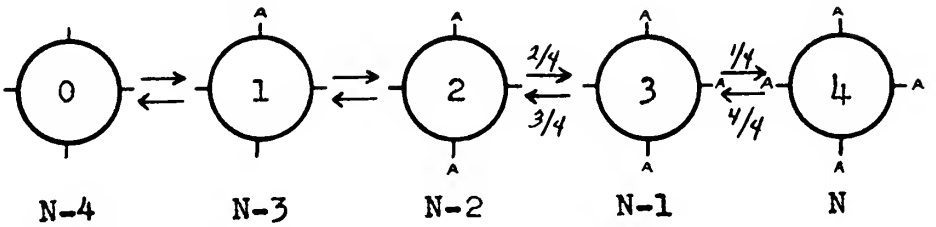
$$\frac{k_3^1}{k_4^1} = \frac{(N-n+1)(n+1)}{(N-n)\,n} = \frac{(4-3+1)(3+1)}{(4-3)\,3} = \frac{2 \times 4}{3} = 8/3$$

Results achieved using the N-pronged statistical model agree exactly with ratios obtained from use of equation (4) above; this agreement lends credence to Bjerrum's calculation of the statistical effect (9).

Formula

$$\frac{k'_n}{k'_{n+1}} = \frac{k'_3}{k'_4} = \frac{(N-n+1)(n+1)}{(n-n)(n)} = \frac{(4-3+1)(3+1)}{(4-3(3)} = \frac{2 \times 4}{1 \times 3} = 8/3$$

N-pronged model



Tendency to form species #3

2 → 3	2/4
4 → 3	4/4

Tendency to destroy species #3

3 → 4	1/4
3 → 2	3/4

$$\text{Ratio} = \frac{2/4 \times 4/4}{1/4 \times 3/4} = 8/3 = \frac{k'_3}{k'_4}$$

Figure 1

Method of Obtaining $\frac{k'_3}{k'_4}$ Using N-Pronged Model Where N=4

For complex systems where N = 6, e.g. Co(II)-NH_3, the 6-pronged model (see Figure 2) shows that

$$\frac{k_3'}{k_4'} = \frac{4/6 \times 4/6}{3/6 \times 3/6} = 16/9$$

which again results from a treatment based on species 3. Comparison with equation (4) shows the same result:

$$\frac{k_3'}{k_4'} = \frac{(N-n+1)(n+1)}{(N-n)\ n} = \frac{(6-3+1)(3+1)}{(6-3)(3)} = \frac{4 \times 4}{3 \times 3} = \frac{16}{9}$$

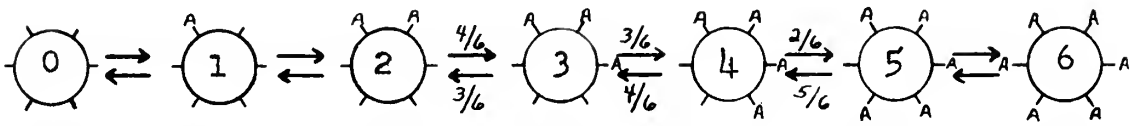
See Appendix II for the complete N-pronged model derivation of $\frac{k_n'}{k_{n+1}'}$ for six coordinate position systems.

The reader is referred to Appendix III for the derivation of the statistical effect in systems where each ligand occupies two coordination positions; i.e. bidentate systems.

Formula

$$\frac{k'_n}{k'_{n+1}} = \frac{k'_3}{k'_4} = \frac{(N-n+1)(n+1)}{(N-n)(n)} = \frac{(6-3+1)(3+1)}{(6-3)(3)} = \frac{16}{9}$$

N-pronged model



N-6 N-5 N-4 N-3 N-2 N-1 N-0

Tendency to form species #3

2 → 3	4/6
4 → 3	4/6

Tendency to destroy species #3

3 → 4	3/6
3 → 2	3/6

$$\text{Ratio} = \frac{4/6 \times 4/6}{3/6 \times 3/6} = \frac{16}{9} = \frac{k'_3}{k'_4}$$

Figure 2

Method of Obtaining $\frac{k'_3}{k'_4}$ Using N-Pronged Model N=6

C. The Ligand Effect

The purpose of this study was to attach quantitative significance to the ligand effect, and for this purpose all calculations were based on the theoretical ratios of $\frac{k'_n}{k'_{n+1}}$ calculated from equation (5). It was assumed that the amount of departure of experimental complexity constants from calculated complexity constants would be a useful quantitative measure of the ligand effect.

The following arbitrary steps were taken at this point:

1) Variations in the complexity constant from one metal ion to another were assumed to result from differences in the ligand effect, rather than from differences in overall coordination potential of the metal ion.
2) Equation (5) for the statistical effect was used to obtain successive values of log k_{n+1} from log k_1 which was assumed as a starting point. A value for each log k_{n+1} was calculated from the previous experimental log k_n. This procedure ruled out any snow-balling of errors in the calculated log k_{n+1} values since at each calculation it was tied in with the experimental value of log k_n and would represent only the statistical effect for that step under the conditions prevailing in the system.
3) Differences in overall coordination potential were compensated for by a normalization technique, whereby

the sum of the logrithims of the calculated consecutive complexity constants ($\sum_{n=1}^{n=N} \log k_n$) by multiplication by a suitable factor was made to equal the sum of the logrithims of the observed consecutive complexity constants.

4) Subtraction of calculated values of $\log k_n'$ from observed values produced a number which it was felt was a useful quantitative measure of the ligand effect. The value obtained was named the Pseudo-Ligand Effect.

Detailed consideration of the results of this method (Appendix IV) showed that some or all of the method was faulty. It became apparent that the normalization technique (step 3 above) was invalid and unwarranted. The principle behind this conclusion may be indicated by asking the question, "Must the sum of the statistical effects equal the sum of the observed effects?". The answer is, "No, that it need not necessarily equal the sum of the observed effects." In fact, the sums would be equal only in a very special and limited case not thus far observed (see equation (6) above and subsequent discussion).

Therefore normalization as described in step 3 above was dispensed with and the ligand effect computed on the basis of steps 1, 2 and 4. The ligand effect determined in this manner is tabulated in Appendix V for the following systems:

$Co^{+2} + 6NH_3$	Table 15
$Ni^{+2} + 6NH_3$	Table 16
$Co^{+3} + 6NH_3$	Table 17
$Cd^{+2} + 6NH_3$	Table 18

Comparison of the "ligand effect" as reported in Appendix V with the rest effect, Table 4 page 57 of Bjerrum (9) discloses that the figures are identical. These calculations have confirmed Bjerrum's figures. In the previous general discussion of the ligand effect, it was shown that $L_{n,n+1} = R_{n,n+1}$ in systems where the ligand is neutral (i.e. $E_{n,n+1} = 0$).

1. Summary

1. Values for Bjerrum's rest effect have been confirmed in certain selected systems (see Appendix V).

2. It is believed that individual complexity constants cannot be separated into a statistical and a ligand effect.

3. Separation of the logrithim of the ratio of the consecutive complexity constants into a statistical effect, a ligand effect and/or a rest effect is possible and feasible.

D. Relative Abundance of the Separate Complex Compounds

Once having determined the successive complexity constants of a system at a given temperature and pressure, an investigation into the relative abundance of the separate complex compounds can be instituted for different concentration conditions. This procedure is enlightening for it provides the quantitative answer to the question of how much of a given compound is present in solution.

Derivation of formula for Aj

With Bjerrum (9) we define

$$a_j = \frac{(MA_j)}{C_M} \qquad (12)$$

where a_j = degree of formation of the indicated separate compound usually on a mole fraction present basis. Therefore $\sum_{j=0}^{j=N} a_j = 1$.

C_M = total concentration of metal M, both free and combined.

(MA_j) = concentration of compound MA_j

for the reaction

$$M + A_j \rightarrow MA_j \qquad (13)$$

where the complexity constant is

$$K_j = \frac{(MA_j)}{(M)\ (A)^j}$$

where parentheses are used to indicate concentration. Then it follows that

$$C_M = (M) + (MA) + (MA_2) + (MA_3) + (MA_4) \qquad (14)$$

for a system where $N = 4$

and by equation (12)

$$a_j = \frac{(MA_j)}{(M) + (MA) + (MA_2) + (MA_3) + (MA_4)} \qquad (15)$$

Since

$$k_1 = \frac{(MA)}{(M)(A)} \quad (16a) \qquad k_3 = \frac{(MA_3)}{(MA_2)(A)} \quad (16c)$$

$$k_2 = \frac{(MA_2)}{(MA)(A)} \quad (16b) \qquad k_4 = \frac{(MA_4)}{(MA_3)(A)} \quad (16d)$$

Solution of equation (16) for (MA), (MA_2), (MA_3) and (MA_4) results in:

$$(MA) = k_1 (M)(A) \tag{17a}$$
$$(MA_2) = k_2 (MA)(A) = k_1k_2 (M)(A)^2 \tag{17b}$$
$$(MA_3) = k_3 (MA_2)(A) = k_1k_2k_3 (M)(A)^3 \tag{17c}$$
$$(MA_4) = k_4 (MA_3)(A) = k_1k_2k_3k_4 (M)(A)^4 \tag{17d}$$

making the indicated substitutions equation (15) becomes

$$a_j = \frac{(MA_j)}{(M) + k_1(M)(A) + k_1k_2(M)(A)^2 + k_1k_2k_3(M)(A)^3 + k_1k_2k_3k_4(M)(A)^4} \tag{18}$$

factoring (M) out of the denominator

$$a_j = \frac{(MA_j)}{(M)(1 + k_1A + k_1k_2(A)^2 + k_1k_2k_3(A)^3 + k_1k_2k_3k_4(A)^4)} \tag{19}$$

Let $\sum_{i=1}^{i=N} K_1(A)^1 = k_1(A) + k_1k_2(A)^2 + k_1k_2k_3(A)^3 + k_1k_2k_3k_4(A)^4$ (20)

then equation (19) becomes

$$a_j = \frac{(MA_j)}{(M)(1 + \sum_{i=1}^{i=N} K_1(A)^1)} \tag{21}$$

Evaluation of equation (21) by insertion of equations (17) for the numerator results in:

$$a_1 = \frac{k_1(M)(A)}{(M)(1 + \sum_{i=1}^{i=N} K_1(A)^1)} = \frac{k_1(A)}{1 + \sum_{i=1}^{i=N} K_1(A)^1} \tag{22a}$$

$$a_2 = \frac{k_1k_2(M)(A)^2}{(M)(1 + \sum_{i=1}^{i=N} K_1(A)^1} = \frac{k_1k_2(A)^2}{1 + \sum_{i=1}^{i=N} K_1(A)^1} \tag{22b}$$

$$a_3 = \frac{k_1k_2k_3(M)(A)^3}{(M)(1 + \sum_{i=1}^{i=N} K_1(A)^1)} = \frac{k_1k_2k_3(A)^3}{1 + \sum_{i=1}^{i=N} K_1(A)^1} \tag{22c}$$

$$a_4 = \frac{k_1k_2k_3k_4(M)(A)^4}{(M)(1+\sum_{i=1}^{i=N} K_i(A)^i} = \frac{k_1k_2k_3k_4(A)^4}{1+\sum_{i=1}^{i=N} K_i(A)^i} \qquad (22d)$$

and a_o = degree of formation of remaining free, uncomplexed metal

$$a_o = 1-\sum_{i=1}^{i=N} a_i \qquad (23)$$

In order to be able to write a generalized formula for a_j, we note similarities in the numerator of equations (22) and let

$$K_j(A)^j = k_1k_2k_3 \ldots k_j(A)^j \qquad (24)$$

and

$$a_j = \frac{K_j(A)^j}{1+\sum_{i=1}^{i=N} K_i(A)^i} \qquad (25)$$

where

j = number representing designated complex compound

$K_j = k_1k_2k_3k_4 \ldots k_j$

$\sum_{i=1}^{i=N} K_i(A)^i = k_1(A) + k_1k_2(A)^2 + k_1k_2k_3(A)^3 \ldots + k_1k_2k_3 \ldots k_N(A)^N$

N = maximum coordination number

It must be pointed out that Sullivan and Hindman (44) have made an unfortunate mistake either in notation or in principle in equation (18) of their article. They give the following expression for a_j:

$$a_j = \frac{(MA_j)}{C_M} = \frac{B_j(A)^j}{1+\sum_{i=1}^{i=N} B_j(A)^i}$$

where B_j is same expression as K_j in this paper. If j is meant to be any running number, the summation term in the denominator is incorrect except for the N^{th} complex compound. Typical relative abundance tables for selected systems have been calculated and are included as Appendix VI.

III. Consecutive Complexity Constants Compiled

The most prevalent complex systems are those in which ammonia or an aliphatic amine is coordinated with a transition metal ion. However, Spike and Parry (42) report that of the metal-methylamine systems investigated (Cd^{+2}-Me, Zn^{+2}-Me, Cu^{+2}-Me, Ni^{+2}-Me and Co^{+2}-Me) only the cadmium ion could be used satisfactorily to obtain complexity constants due to the fact that in all systems, except Cd^{+2}-Me, methylamine caused precipitation of the hydroxide before soluble coordination compounds containing two molecules of methylamine were formed. Bjerrum and Lamm (11) using highly concentrated methylamine solutions obtained values for the dissociation constant of tetrakismethylaminecupric (II) ion which were twenty to twenty-five times as great as the corresponding complexity constant for the tetraamminecupric(II) ion.

Several investigators have postulated steric hindrance or steric factors to explain the irregularities in the consecutive complexity constants (5). Correlation of the base strength of an amine with the complexity constants has been attempted, but several irregularities in the complexity constants so correlated remain unexplained (4), (5), (10). On the other hand, many investigators have held that an increase in the difference between consecutive complexity constants may be ascribed to the greater steric hindrance afforded by coordinated amine molecules as compared with coordinated water molecules of hydration (3),(5),(18),(19), (45),(46).

A search of the literature has been made in order to compile the most accepted values for the consecutive complexity constants for selected metal ions. Particular attention has been paid to systems where the coordinated ligand is neutral and where the coordinated electron pair is donated by the nitrogen atom of the ligand.

It was found difficult to obtain data in metal amine systems where structurally different amines had been systematically coordinated with the same metal ion. Douglas, Laitiner and Bailar (14) working polarographically with Cd^{+2} and structurally dissimilar amines and Basolo and Murmann (5) working with N,N' dialkylethylenediamines have used this plan. Many investigators have reported work where the metal ion was varied systematically and the amine kept constant. In this field the work of Bjerrum (9), Carlson, McReynolds and Meibohm (24) and Schwarzenbach et al (38), (39),(40),(41) is outstanding.

The consecutive complexity constants gleaned from the literature are compiled in the following tables. In subsequent sections these constants will be used without reference to the source from which taken.

Abbreviations Used in Tables and Subsequent Discussion

Abbreviation	Meaning
Bu	n-butyl radical
dien	diethylenetriamine
dipy	α, α'-dipyridyl
en	ethylenediamine
Et	ethyl radical
Me	methyl radical
o-phen	orthophenanthroline
n-pr	n-propyl radical
pr	propylenediamine
ptn	triaminopropane
py	pyridine
tren	triaminotriethylamine
trien	triethylenetetramine

Table 1

Complexity Constants of Fe^{+2} and Selected Amines

System	log k_1	log k_2	log k_3	References
Fe(II) + 3 dipy	4.20	<5.0	>7.3	(6)(7)(8)(38)
Fe(II) + 3 o-phen	5.88	?	21.3*	(25)(31)(32)
Fe(II) + 3 en	4.28	3.25	1.99	(9)
Fe(II) + 2 dien	6.23	4.13		(24)
Fe(II) + 2 trien	8.31	3.92		(24)(41)
Fe(II) + 1 tren	8.78			(2)

* log K_3 = log k_1 + log k_2 + log k_3

Table 2

Complexity Constants of Cu^{+2} and Selected Amines

System	log k_1	log k_2	log k_3	log k_4	References
Cu(II) + $4NH_3$	4.15	3.50	2.89	2.13	(9)(10)(43)
Cu(II) + $4NH_2CH_3$				(1.73-1.83)	(11)(42)
Cu(II) + $4NH_2Bu$				(1.73-1.83)	(11)
Cu(II) + 2 dipy		14.2*			(36)
Cu(II) + 2 o-phen					(36)
Cu(II) + 2 en	10.55	9.05			(13)(5)(9)(10)(30)(43)
Cu(II) + 2 pr	10.58	9.08			(13)(30)
Cu(II) + 2 dien	16.11	7.3			(22)(24)(30)
Cu(II) + 1 trien	20.62				(23)(24)(39)(41)
Cu(II) + 1 tren	18.98				(2)(38)
Cu(II) + 2 ptn	11.1	9.0			(40)
Cu(II) + N,N'-diMe-en	10.47	7.63			(5)
Cu(II) + N,N'-diEt-en	9.30	6.32			(5)
Cu(II) + N,N'-di n-pr en	8.79	5.55			(5)
Cu(II) + N,N'-diBu en	8.67	4.84			(5)

* log K_2 = log k_1 + log k_2

Table 3

Complexity Constants of Zn^{+2} and Selected Amines

System	log k_1	log k_2	log k_3	log k_4	References
Zn(II) + $4NH_3$	2.37	2.44	2.50	2.15	(9)(15)(16)(43)
Zn(II) + $4NH_2CH_3$					(42)
Zn(II) + 4 py	1.42±0.3	-0.30±0.3	0.49±0.7	0.32±0.3	(17)(20)(21)(35)
Zn(II) + 3 o-phen	6.43	5.72	4.85		(26)
Zn(II) + 3 en	5.71	4.66	1.72		(13)(43)
Zn(II) + 3 pr	5.89	4.98	1.70		(13)
Zn(II) + 2 dien	8.9	5.5			(24)(39)
Zn(II) + 1 trien	11.94				(24)(41)
Zn(II) + 1 tren	14.65				(2)(38)
Zn(II) + 1 ptn	6.75				(40)

Table 4

Complexity Constants of Cd^{+2} and Selected Amines

System	log k_1	log k_2	log k_3	log k_4	References
Cd(II) + $4NH_3$	2.65	2.10	1.44	0.93	(9)(10)(15)(16)(42)
Cd(II) + $4NH_2CH_3$	2.745	2.06	1.13	0.61	(27)(42)
Cd(II) + 4 py		2.14*		2.554	(14)
Cd(II) + 3 dipy			10.49*		(14)
Cd(II) + 3 o-phen		13.156*	2.04		(14)
Cd(II) + 3 en	5.84	4.78	2.07		(13)(14)(42)
Cd(II) + 3 pr	5.42	4.55	2.15		(13)(14)
Cd(II) + 2 dien	8.45	5.4			(14)(39)(41)
Cd(II) + 2 trien	10.79	3.07			(14)(24)
Cd(II) + 1 ptn	6.45				(40)

* $\log K_n = \log k_1 + \ldots + \log k_n$

IV. The Rest Effect

A. Introduction

It was decided to use Bjerrum's Rest Effect to show variation in a system where structurally different amines had been systematically coordinated with the same metal ion. Ideally an investigation of this type should include a systematic variation of ligand in the following manner:

a. Metal-ammonia
b. Metal-aliphatic amine
c. Metal-aromatic amine
d. Metal-heterocylic nitrogen compound
e. Metal-chelating amine.

Consecutive complexity constants for metal-ligand systems of type a, d and e have been reported in the literature. Consecutive complexity constants for metal-aliphatic amine and metal-aromatic amine systems have not been as thoroughly reported and the data are indeed meager in these two categories.

A few basic equations treated previously will be repeated here for ready reference.

$$L_{n,n+1} = T_{n,n+1} - S_{n,n+1} = \log \frac{k_n}{k_{n+1}} - S_{n,n+1} \quad (1)$$

In words, the ligand effect ($L_{n,n+1}$) is equal to the logrithim of the ratio of consecutive complexity constants minus the statistical effect ($S_{n,n+1}$).

Also by definition

$$L_{n,n+1} = E_{n,n+1} + R_{n,n+1} \qquad (2)$$

or

$$L_{n,n+1} = R_{n,n+1} \text{ if } E_{n,n+1} = 0 \qquad (3)$$

In equation (2), the ligand effect is defined as being equal to the sum of the electrostatic effect ($E_{n,n+1}$) plus the rest effect ($R_{n,n+1}$). For systems where the ligand is unchanged, $E_{n,n\ 1}$ is defined as being zero and equation (3) results where the ligand effect is equal to the rest effect. Equating expressions equal to the ligand effect, equations (1) and (3), equation (4) is obtained:

$$R_{n,n+1} = \log \frac{k_n}{k_{n+1}} - S_{n,n+1} \qquad (4)$$

where $R_{n,n+1}$ is the rest effect. $S_{n,n+1}$ is the statistical effect and obtained as indicated in Section II of this paper. The term $\log \frac{k_n}{k_{n+1}}$ is the logrithim of the ratio of experimental consecutive complexity constants.

Equation (4) was used to evaluate the rest effect by inserting appropriate values for k_n and k_{n+1} from Tables 1, 2, 3 and 4 and for $S_{n,n+1}$ as indicated in Section II. Detailed calculations leading to results reported later in this section appear in Appendix VII.

B. Variation of the Rest Effect with the Coordinated Amine

Table 5

The Rest Effect in Selected Copper(II) Amine Systems
Cu(II)

System	$R_{1,2}$	$R_{2,3}$	$R_{3,4}$	References
Cu(II) + $4NH_3$	0.22	0.26	0.33	(9)
Cu(II) + 2 pr*	0.60			
Cu(II) + 2 en	0.65			
Cu(II) + 2 N,N'-di Me en	1.94			
Cu(II) + 2 N,N'-di Et en	2.08			
Cu(II) + 2 N,N'-di n-pr en	2.34			
Cu(II) + 2 N,N'-di Bu en	2.93			

* Same abbreviations used here and in following tables as used in Tables 1, 2, 3 and 4.

Bjerrum (9) characterizes the Cu(II)-NH_3 system as the complex system in which the consecutive complexity constants, for various reasons, are known with the greatest degree of certainty and observes that the rest effect increases continually with the number of ammonia molecules coordinated. The values for $R_{1,2}$, $R_{2,3}$ and $R_{3,4}$ reported in Table 6 agree substantially with those reported by Bjerrum. He further states that $R_{4,5}$ cannot be calculated even though k_5 is known since an asymmetry occurs in this step and the normal statistical expressions do not adequately represent this asymmetry.

It is to be noted that $R_{1,2}$ increases as larger alkyl groups are substituted at the two nitrogen atoms in the ethylenediamine molecules. This systematic increase can be ascribed to steric hindrance which operates to reduce k_2

as the size of the substituted alkyl group is increased (3), (5),(18),(19),(45),(46).

Use of the Pauling-Slater extension of the Heitler-London orbital theory indicates that the electronic configuration of the cupric ion leaves one unpaired electron in a 3d orbital. This might suggest sp^3 bond hybridization, but Pauling (37) points out that placing the unpaired electron in an empty 4p orbital requires no loss of energy. Hence the stronger dsp^2 planar bonding might result. X-ray studies indicate that this is the case and that copper(II) complexes are indeed planar in arrangement (34).

Table 6

The Rest Effect in Selected Zinc(II) Amine Systems
Zn(II)

System	$R_{1,2}$	$R_{2,3}$	$R_{3,4}$	References
Zn(II) + $4NH_3$	-0.50	-0.41	-0.08	(9)
Zn(II) + 4 py	1.29*	-1.14*	-0.26*	
Zn(II) + 3 en	0.37	1.97**		
Zn(II) + 3 o-phen	0.03	-0.10**		
Zn(II) + 3 pr	0.23	2.31**		

* Based on average values for log k_n. See Appendix VII.
** Assuming chelation of three molecules of bidentate ligand.

Table 7

The Rest Effect in Selected Zinc(II) Bidentate Systems
Zn(II)

System	$R_{1,2}$	$R_{2,3}$
Zn(II) + 3 en	0.45	2.46
Zn(II) + 3 o-phen	0.11	0.39
Zn(II) + 3 pr	0.31	2.80

The values in Table 7 are calculated on the assumption that first molecule chelates and second and third molecules do not.

In Zn(II)-bidentate systems it would be expected that only two molecules would be coordinated since according to the Pauling-Slater extended orbital theory only the 4s and three 4p orbitals are available. Experimental work, however, (9),(10),(13),(26),(43) indicates that instead three bidentate molecules are actually coordinated. This problem may be approached in two different ways. First, it may be assumed that all three bidentate molecules are chelated. This solution means that there are two more orbitals available for bounding. This may be interpreted to mean an availability of two 4d orbitals for coordinate covalent bonding. Second, it may be assumed the first bidentate molecule chelates whereas the second and third bidentate molecules do not (i.e. are coordinately bound only through one amine group).

Table 7 tabulates the rest effects for Zn(II)-amine systems where it is assumed that the second and third bidentate groups are coordinately bound only through one amine group. In comparing Tables 6 and 7 it should be noted that:

a) $R_{1,2}$ in Table 7 is about 0.1 unit greater than in Table 6.

b) $R_{2,3}$ in Table 7 is about 0.5 unit greater than in Table 6.

c) $R_{2,3}$ in Z(II)-o-phen system is positive in Table 7 as contrasted with a negative value in Table 6.

As a consequence it is suggested that in the zinc(II)-bidentate systems tabulated in Table 7 only the first bidentate ligand chelates and that the second and third are coordinately bound through only one amine group.

Table 8

The Rest Effect in Selected Cadmium(II) Amine Systems
Cd(II)

System	R1,2	R2,3	R3,4	References
$Cd(II) + 6NH_3$	0.12	0.31	0.08	(9)
$Cd(II) + 4NH_2CH_3$	0.25	0.58	0.09	
Cd(II) + 3 en	0.38	1.74*		
Cd(II) + 3 pr	0.19	1.43*		

* Assuming chelation of three molecules of bidentate ligand.

Table 9

The Rest Effect in Selected Cadmium(II) Bidentate Systems

System	R1,2	R2,3
Cd(II) + 3 en	0.46	2.23
Cd(II) + 3 pr	0.27	1.92

In general the remarks made previously concerning zinc(II)-amine systems apply qualitatively to cadmium(II)-amine systems. With the cadmium(II) ion it would be expected that only $5s5p^3$ orbitals are available. In the cadmium(II)-ammonia system six ammonia molecules are coordinated but after the binding of the fourth molecule of ammonia an

asymmetry occurs which precludes further consideration of the subsequent coordination as following any statistical consideration (9). Therefore only $R_{1,2}$, $R_{2,3}$ and $R_{3,4}$ have been calculated for this system as the expressions for the statistical uptake of the fifth and sixth ammonia molecules are unknown.

Computation of the rest effect in the cadmium(II)-ammonia system produces values which agree substantially with those reported by Bjerrum (9).

In Table 9 are shown values for the rest effect based on the assumption that the first bidentate molecule chelates whereas the second and third bidentate molecules do not. Points to note in comparing Tables 8 and 9 are:

a) $R_{1,2}$ in Table 9 in about .1 unit greater than in Table 8.

b) $R_{2,3}$ in Table 9 is about .5 unit greater than in Table 8.

Since the evidence is the same the same suggestion made with reference to zinc(II)-bidentate systems is made with regard to cadmium(II)-bidentate systems; namely that the first bidentate molecule chelates whereas the second and third molecules do not.

Table 10

The Rest Effect in Selected Iron(II)-Amine Systems
Fe(II)

System	R1,2	R2,3	References
Fe(II) + 3 en	0.35	0.29	(9)
Fe(II) + 3 dipy	-1.48*	-3.77*	
Fe(II) + 3 o-phen	-1.70*	-2.57*	

*See discussion.

Computations of the rest effect in the Fe(II)-en system produce values in agreement with those reported by Bjerrum (9).

Since k_2 in the Fe(II)-dipy system is not capable of being determined due to the transitory nature of the bis (dipy) Fe(II) ion (7),(8),(29), it has been assumed that log k_2 order of magnitude is about 5. Log K_3 order of magnitude then becomes about 7.8 in order to reconcile log k_3 with reported values (6),(8). Calculation of the rest effects then proceded on this basis.

In the Fe(II)-o-phen system even more doubt exists as to the correct value for log k_2. Kolthoff, Leussing and Lee (25) report that bis(o-phen) Fe(II) ion is relatively unstable with respect to other Fe(II)-o-phen complex ions and for most quantitative analytical purposes its existence may be neglected. On the basis of structural similarity between α, α'-dipyridyl and orthophenanthroline, it has been assumed that the order of magnitude of log k_2 in the Fe(II)-o-phen system is about 6.9 which requires that log k_3 in this system be about 8.5.

Table 10 shows that $R_{1,2}$ and $R_{2,3}$ for both the Fe(II)-dipy and Fe(II)-o-phen systems are negative and quite large. Since the log k_2 values for both the Fe(II)-dipy and Fe(II)-o-phen systems are in doubt, the rest effects calculated from these doubtful log k values are likewise in doubt. Therefore, values for $R_{1,2}$ and $R_{2,3}$ for these two systems should be regarded only as a guide until more information is available.

The significance of the large negative rest effects is not known but for the three systems available the similarities and differences may be noted. For instance, all three ligands (en, dipy and o-phen) form five member chelate rings with the ferrous ion. On the other hand, the nitrogen atom in the ethylenediamine molecule can be contrasted with the heterocylic nitrogen molecule in α, α'-dipyridyl and in orthophenanthroline.

C. Comments Concerning the Rest Effect

For a number of systems listed in Tables 1, 2, 3 and 4, the rest effect cannot now be computed because the statistical expression for these systems is unknown. This situation is best indicated by data available for systems of metal-dien, metal-trien and metal-tren. On the other hand, much of the data on consecutive complexity constants for systems of metal-dipy, metal-o-phen (12) and metal-py which are of the greatest interest, either have not been investigated or only an overall gross complexity constant has been reported.

In connection with the rest effect in ammonia and ethylenediamine systems with Cu(I), Ag(I), Hg(II), Cu(II), Zn(II), Cd(II), Mn(II), Fe(II), Ni(II), Co(II) and Co(III), Bjerrum (p.58, Ref.9) maintains

a) That the rest effect is usually small

b) That it can be either positive or negative

c) That it generally shows slight variation within the same system

d) That it is generally independent of the magnitude of the consecutive complexity constant of the system.

e) That the irregular variation of the values of the rest effect is due to a large extent to experimental uncertainty.

In brief Bjerrum maintains that the rest effect is nothing but a small correction factor.

In view of the discussion of the rest effect presented earlier in this section, exception must be taken to certain of Bjerrum's views concerning the rest effect. First of all, calculations involving a greater diversity of metal-ammine systems have been reported in this paper than were considered by Bjerrum. Inspection of Tables 5 through 10 inclusive shows that values reported here for the rest effect range from -0.50 to 2.31 even accepting the smaller values set down in Tables 6 and 8 over those in Tables 7 and 9. The Fe(II)-dipy, the Fe(II)-o-phen systems have been purposely disregarded due to the assumption made in arriving at the

rest effect and to the doubt as to the actual values for the rest effect in these two systems. The Zn(II)-py rest effects have been disregarded due to lack of certainty with which the consecutive complexity constants are known. In contradiction to item a) of Bjerrum's statement, rather large variations in the values that the rest effect may take on have been observed. And in contradiction to item d) it must be maintained that the rest effect is intimately connected with the magnitude of the consecutive complexity constants of the system; e.g. large values of $R_{2,3}$ are found in the Zn(II)-en, Cd(II)-en, Zn(II)-pr and Cd(II)-pr systems because in each case log k_3 is much less than is log k_2 (see Tables 3, 4, 6 and 8).

Bjerrum has not speculated upon the mathematical form of the rest effect because his investigation led him to the conclusion that the rest effect was a small correction factor. On the other hand, it has been shown in this paper that the rest effect need not be small.

It is suggested that the rest effect is a log function of such nature that it may be represented as a ratio of the contribution from the n^{th} species divided by the contribution from the $(n+1)^{th}$ species. Thus

$$R_{n,n+1} = \log \frac{r_n}{r_{n+1}} \qquad (5)$$

The statistical effect, $S_{n,n+1}$, may be considered to be the log of a ratio of statistical consecutive complexity

constants. If this substitution is made in the expression for $R_{n,n\,1}$, the following expression results:

$$R_{n,n+1} = T_{n,n+1} - S_{n,n+1} = \log \frac{k_{ne}}{k_{n+1e}} - \log \frac{k_{ns}}{k_{n+1s}} \qquad (6)$$

where subscript e refers to experimentally determined constants and subscript s refers to statistically determined constants. Equating equals results in

$$\log \frac{r_n}{r_{n+1}} = \log \frac{k_{ne}}{k_{n+1e}} - \log \frac{k_{nT}}{k_{n+1T}} \qquad (7)$$

and if $R_{n,n+1}$ is truly a log function as suggested, even small values of $R_{n,n+1}$ take on a greater significance from that indicated by Bjerrum's correction factor.

D. Summary

1. It has been suggested that the mathematical form of the rest effect is a log function of the type

$$R_{n,n+1} = \log \frac{r_n}{r_{n+1}}$$

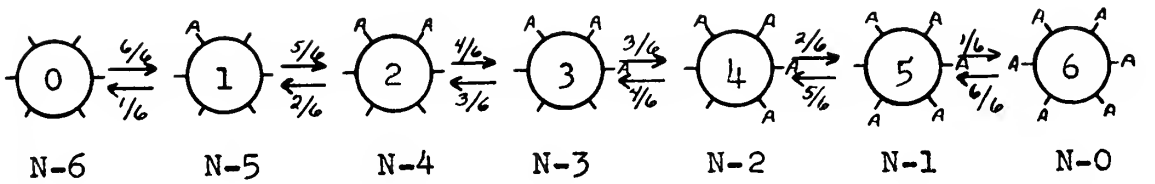
2. It has been suggested that anomalies in the number of bidentate molecules coordinated in the zinc(II) amine and cadium(II) amine systems can be explained by assuming that the first bidentate molecule chelates with the metal ion and that the second and third molecules are coordinately bound through only one of the two possible amine groups.

3. It has been noted that $R_{1,2}$ increases as the size of the substituted alkyl group increases when N,N' dialkylethylenediamines are complexed with Cu(II) ion.

APPENDIX I - Symbols

A	ligand molecule
a_o	degree of formation of free, uncomplexed metal
a_1	degree of formation of separate complex compound MA
a_j	degree of formation of separate complex compound MAj
C_M	total concentration of metal M in solution
$E_{n,n+1}$	electrostatic effect
k	consecutive complexity constant
k_1	consecutive complexity constant for reaction $M + A \rightarrow MA$ where $k_1 = \frac{(MA)}{(M)(A)}$
k_n	consecutive complexity constant for reaction $M + nA \rightarrow MA_n$ $k_n = \frac{(MA_n)}{(MA_{n-1})(A)}$ $n = 1,2, \ldots N$
k'_n	statistical complexity constant
K_N	total overall complexity constant $K_N = k_1k_2k_3k_4 \ldots k_N$
$L_{n,n+1}$	ligand effect
M	metal molecule, in this paper considered to be one of the transition metals
N	maximum coordination number
n	number of molecules coordinated with the metal ion in a coordination complex, n = 1,2,3 .... N
$R_{n,n+1}$	rest effect
$S_{n,n+1}$	statistical effect
$T_{n,n+1}$	total effect

APPENDIX II - Complete N-Pronged Model Derivation for N=6



Tendency to form species #1

$0 \rightarrow 1 \quad 6/6$
$2 \rightarrow 1 \quad 2/6$

Tendency to destroy species #1

$1 \rightarrow 0 \quad 1/6$
$1 \rightarrow 2 \quad 5/6$

$$\text{Ratio} = \frac{6/6 \times 2/6}{1/6 \times 5/6} = \frac{12}{5} = \frac{k1}{k2}$$

Tendency to form species #2

$1 \rightarrow 2 \quad 5/6$
$3 \rightarrow 2 \quad 3/6$

Tendency to destroy species #2

$2 \rightarrow 1 \quad 2/6$
$2 \rightarrow 3 \quad 4/6$

$$\text{Ratio} = \frac{5/6 \times 3/6}{2/6 \times 4/6} = \frac{15}{8} = \frac{k2}{k3}$$

Tendency to form species #3

$2 \rightarrow 3 \quad 4/6$
$4 \rightarrow 3 \quad 4/6$

Tendency to destroy species #3

$3 \rightarrow 4 \quad 3/6$
$3 \rightarrow 2 \quad 3/6$

$$\text{Ratio} = \frac{4/6 \times 4/6}{3/6 \times 3/6} = \frac{16}{9} = \frac{k3}{k4}$$

Figure 3

Tendency to form species #4

$3 \rightarrow 4 \quad 3/6$
$5 \rightarrow 4 \quad 5/6$

Tendency to destroy species #4

$4 \rightarrow 5 \quad 2/6$
$4 \rightarrow 3 \quad 4/6$

$$\text{Ratio} = \frac{3/6 \times 5/6}{2/6 \times 4/6} = \frac{15}{8} = \frac{k4}{k5}$$

Tendency to form species #5

$4 \rightarrow 5 \quad 2/6$
$6 \rightarrow 5 \quad 6/6$

Tendency to destroy species #5

$5 \rightarrow 6 \quad 1/6$
$5 \rightarrow 4 \quad 5/6$

$$\text{Ratio} = \frac{2/6 \times 6/6}{1/6 \times 5/6} = \frac{12}{5} = \frac{k5}{k6}$$

APPENDIX III - Statistical Effect in Bidentate Systems

For a metal ion-bidentate amine system where four coordination positions are available, there are four ways of coordinating the first bidentate molecule and only one way of coordinating the second bidentate molecule. Since the tendency of compound MA_n to split off a molecule is proportional to the number of ligands bound, or n, the following ratios are obtained:

$$4/1:1/2$$

and

$$\frac{k_1}{k_2} = \frac{4/1}{1/2} = 8 \qquad \text{or} \qquad S_{1,2} = \log 8 = 0.904$$

In a coordination system where only four positions are available, it is possible that the first bidentate molecule will chelate but the second and third bidentate molecules will coordinate to the central metal ion through only one amine group. In this situation, the above ratios are modified to

$$4/1:2/2:1/3$$

and

$$\frac{k_1}{k_2} = \frac{4/1}{2/2} = 4 \qquad \text{and} \qquad S_{1,2} = \log 4 = 0.602$$

$$\frac{k_2}{k_3} = \frac{2/2}{1/3} = 3 \qquad S_{2,3} = \log 3 = 0.477$$

When bidentate ligands coordinate with ions capable of accepting six amine ligands, stereochemically there are twelve ways the first molecule may coordinate, five ways the second molecule may coordinate and only one way the third amine molecule may coordinate. Since the tendency to split off a molecule is proportional to the number of ligands coordinated, the ratios of the consecutive complexity constants are:

$$12/1:5/2:1/3$$

If there is steric hindrance for the third group to coordinate, the ratio for the third group must be modified to show this (9) and the following ratios result:

$$12/1:5/2:4/15$$

and the statistical effect for three coordinated bidentate ligands is:

$$S_{1,2} = \log \frac{12/1}{5/2} = \log \frac{24}{5} = 0.682$$

$$S_{2,3} = \log \frac{5/2}{4/15} = \log \frac{75}{8} = 0.972$$

APPENDIX IV - Pseudo Ligand Effect Tables

Table 11

Pseudo Ligand Effect Co(II)-NH_3 System

n	Experimental log kn	Unnormalized log kn	Normalized log kn	Pseudo-Ligand Effect
1	2.11	2.11	1.720	0.39
2	1.63	1.73	1.410	0.22
3	1.05	1.358	1.105	-0.055
4	0.76	0.800	0.651	0.109
5	0.18	0.488	0.398	-0.218
6	-0.62	-0.200	-0.164	-0.456
Sum	5.11	6.286	5.120	

Table 12

Pseudo Ligand Effect Ni(II)-NH_3 System

n	Experimental log kn	Unnormalized log kn	Normalized log kn	Pseudo-Ligand Effect
1	2.80	2.80	2.46	0.34
2	2.24	2.42	2.12	0.12
3	1.73	1.97	1.73	0
4	1.19	1.48	1.30	-0.11
5	0.75	0.92	0.806	-0.056
6	0.03	0.37	0.324	-0.294
Sum	8.74	9.96	8.740	

Table 13

Pseudo Ligand Effect Co(III)-NH_3 System

n	Experimental log k_n	Unnormalized log k_n	Normalized log k_n	Pseudo-Ligand Effect
1	7.3	7.3	7.05	.25
2	6.7	6.92	6.68	.02
3	6.1	6.43	6.21	-.11
4	5.6	5.85	5.65	-.05
5	5.05	5.33	5.15	-.10
6	4.41	4.67	4.51	-.10
Sum	35.21	36.50	35.25	

Table 14

Pseudo Ligand Effect Cd(II)-NH_3 System

n	Experimental log k_n	Unnormalized log k_n	Normalized log k_n	Pseudo-Ligand Effect
1	2.65	2.65	1.72	0.93
2	2.10	2.27	1.48	0.62
3	1.44	1.83	1.19	0.25
4	0.93	1.19	0.77	0.157
5	-0.32	0.66	0.43	-0.75
6	-1.66	-0.70	-0.456	-1.204
Sum	5.14	7.90	5.137	

APPENDIX V - Calculated Ligand Effect

Table 15

Calculated Ligand Effect Co(II)-NH_3 System

n	Experimental log k_n	Calculated log k_n	Ligand Effect
1	2.11	2.11	0
2	1.63	1.73	0.10
3	1.05	1.36	0.31
4	0.76	0.80	0.04
5	0.18	0.49	0.31
6	-0.62	-0.20	0.42
Sum	5.11	6.29	

Table 16

Calculated Ligand Effect Ni(II)-NH_3 System

n	Experimental log k_n	Calculated log k_n	Ligand Effect
1	2.80	2.80	0
2	2.24	2.42	0.18
3	1.73	1.97	0.24
4	1.19	1.48	0.29
5	0.75	0.92	0.17
6	0.03	0.37	0.34
Sum	8.74	9.96	

Table 17

Calculated Ligand Effect Co(III)-NH_3 System

n	Experimental log kn	Calculated log kn	Ligand Effect
1	7.3	7.3	0
2	6.7	6.92	0.22
3	6.1	6.43	0.33
4	5.6	5.85	0.25
5	5.05	5.33	0.28
6	4.41	4.67	0.26
Sum	35.21	36.50	

Table 18

Calculated Ligand Effect Cd(II)-NH_3 System

n	Experimental log kn	Calculated log kn	Ligand Effect
1	2.65	2.65	0
2	2.10	2.27	0.17
3	1.44	1.83	0.39
4	0.93	1.19	0.26
5	-0.32	0.66	0.98
6	-1.66	-0.70	0.96
Sum	5.14	7.90	

APPENDIX VI - Tabulated Relative Abundance of the Separate Compounds

The relative abundance of the separate complex compounds has been calculated using equation (25) of Section III. Successive complexity constants for ammonia, ethylenediamine, diethylenetriamine and triethylenetetramine as found in the literature were used in these calculations. Relative abundance for the following metal-amine systems were calculated.

Ligand	NH_3	en	dien	trien
Metal	Co(II)	Mn(II)	Mn(II)	Mn(II)
	Co(III)	Fe(II)	Fe(II)	Fe(II)
	Ni(II)	Co(II)	Co(II)	Co(II)
	Cu(II)	Ni(II)	Ni(II)	Ni(II)
	Ag(I)	Cu(II)	Cu(II)	Cu(II)
	Zn(II)		Zn(II)	Zn(II)
	Cd(II)			Cd(II)

Note: en = ethylenediamine
dien = diethylenetriamine
trien = triethylenetetramine

According to equation (25), the relative abundance, a_j, is dependent upon a function of concentration of the ligand. Since this is so, values of a_j are tabulated according to pA where pA = -log A and A is the ligand coordinated to the central metal ion.

Table 19

Calculated Relative Abundances for pA = 4

M (A=NH_3)	a_0	a_1	a_2	a_3	a_4	a_5	a_6	N	References
Co(II)	0.987	0.0127	0	0	0	0	0	6	(b)(d)(e)
Co(III)	0	0	0	0.001	0.024	0.273	0.702	6	(b)(d)
Ni(II)	0.940	0.059	0.001	0	0	0	0	6	(b)(d)(e)
Cu(II)	0.344	0.489	0.155	0.012	0.0002	0		5	(b)(d)
Ag(I)	0.790	0.125	0.085					2	(a)
Zn(II)	0.976	0.023	0.001	0	0			4	(b)(d)
Cd(II)	0.955	0.044	0.001	0	0	0	0	6	(b)(d)(e)

M (A→)	en				Ref.	dien			N	References
	a_0	a_1	a_2	a_3		a_0	a_1	a_2		
Mn(II)	0.949	0.051	0.001	0	(a)	0.490	0.478	0.032	2	(c)(d)
Fe(II)	0.307	0.587	0.104	0.001	(a)	0.005	0.877	0.118	2	(c)(d)
Co(II)	0.001	0.116	0.785	0.0988	(a)	0.002	0.008	0.990	2	(c)(d)
Co(III)										
Ni(II)	0	0.001	0.221	0.778	(a)	0	0.0001	0.9999	2	(c)(d)
Cu(II)	0	0	1.000	0	(b)(d)	0	1.000		1	(c)(d)
Ag(I)										
Zn(II)						0	1.000		1	(c)(d)
Cd(II)										

M (A→)	trien			N	Ref.
	a_0	a_1	a_2		
Mn(II)	0.036	0.902	0.062	2	(c)(d)
Fe(II)	0	0.543	0.457	2	(c)(d)
Co(II)	0	0.806	0.194	2	(c)(d)
Co(III)					
Ni(II)	0.001	0.023	0.976	2	(c)(d)
Cu(II)	0	1.000		1	(c)(d)
Ag(I)					
Zn(II)	0	1.000		1	(c)(d)
Cd(II)	0	0.866	0.134	2	(c)(d)

Table 20

Calculated Relative Abundances for pA = 3

A=NH_3 M	a_0	a_1	a_2	a_3	a_4	a_5	a_6	N	References
Co(II)	0.881	0.114	0.005	0	0	0	0	6	(b)(d)(e)
Co(III)	0	0	0	0	0.0003	0.037	0.963	6	(b)(d)
Ni(II)	0.572	0.362	0.063	0.003	0	0	0	6	(b)(d)(e)
Cu(II)	0.008	0.143	0.451	0.351	0.047	0		5	(b)(d)
Ag(I)	0.075	0.119	0.805					2	(a)
Zn(II)	0.756	0.177	0.049	0.015	0.002			4	(a)
Cd(II)	0.659	0.303	0.037	0.001	0	0	0	6	(b)(d)(e)

A→	en					dien			
M	a_0	a_1	a_2	a_3	Ref.	a_0	a_1	a_2	N	References
Mn(II)	0.626	0.335	0.038	0	(a)	0.056	0.563	0.381	2	(c)(d)
Fe(II)	0.017	0.333	0.592	0.058	(a)	0	0.425	0.575	2	(c)(d)
Co(II)	0	0.006	0.440	0.554	(a)	0.001	0.001	0.998	2	(c)(d)
Co(III)										
Ni(II)	0	0	0.028	0.972	(a)	0	0	1.000	2	(c)(d)
Cu(II)	0	0	0.9999	0.0001	(b)(d)	0	1.000		1	(c)(d)
Ag(I)										
Zn(II)						0	1.000		1	(c)(d)
Cd(II)										

A→	trien				
M	a_0	a_1	a_2	N	Ref.
Mn(II)	0.004	0.588	0.408	2	(c)(d)
Fe(II)	0	0.106	0.894	2	(c)(d)
Co(II)	0	0.294	0.706	2	(c)(d)
Co(III)					
Ni(II)	0	0.002	0.998	2	(c)(d)
Cu(II)	0	1.000		1	(c)(d)
Ag(I)					
Zn(II)	0	1.000		1	(c)(d)
Cd(II)	0	0.392	0.608	2	(c)(d)

Table 21

Calculated Relative Abundances for pA = 2

M (A=NH_3)	a_0	a_1	a_2	a_3	a_4	a_5	a_6	N	References
Co(II)	0.345	0.444	0.189	0.021	0.001	0	0	6	(b)(d)(e)
Co(III)	0	0	0	0	0	0.004	0.996	6	(b)(d)
Ni(II)	0.039	0.251	0.437	0.235	0.036	0.002	0	6	(b)(d)(e)
Cu(II)	0	0.002	0.052	0.402	0.542	0.0016		5	(b)(d)
Ag(I)	0.001	0.015	0.985					2	(a)
Zn(II)	0.017	0.040	0.110	0.346	0.489			4	(a)
Cd(II)	0.075	0.357	0.438	0.120	0.010	0	0	6	(b)(d)(e)

M (A→)	en					dien			N	References
	a_0	a_1	a_2	a_3	Ref.	a_0	a_1	a_2		
Mn(II)	0.077	0.414	0.473	0.036	(a)	0	0.129	0.871	2	(c)(d)
Fe(II)	0	0.028	0.492	0.480	(a)	0	0.069	0.931	2	(c)(d)
Co(II)	0	0	0.074	0.926	(a)	0	0.0001	0.9999	2	(c)(d)
Co(III)										
Ni(II)	0	0	0.003	0.997	(a)	0	0	1.000	2	(c)(d)
Cu(II)	0	0	0.999	0.001	(b)(d)	0	1.000		1	(c)(d)
Ag(I)										
Zn(II)						0	1.000		1	(c)(d)
Cd(II)										

M (A→)	trien			N	Ref.
	a_0	a_1	a_2		
Mn(II)	0.001	0.126	0.873	2	(c)(d)
Fe(II)	0	0.012	0.988	2	(c)(d)
Co(II)	0	0.040	0.960	2	(c)(d)
Co(III)					
Ni(II)	0	0.0002	0.9998	2	(c)(d)
Cu(II)	0	1.000		1	(c)(d)
Ag(I)					
Zn(II)	0	1.000		1	(c)(d)
Cd(II)	0	0.060	0.940	2	(c)(d)

Table 22

Calculated Relative Abundances for pA = 1

A=NH_3 M	a_0	a_1	a_2	a_3	a_4	a_5	a_6	N	References
Co(II)	0.007	0.075	0.320	0.359	0.207	0.031	0.00075	6	(b)(d)(e)
Co(III)	0	0	0	0	0	0.0004	0.9996	6	(b)(d)
Ni(II)	0	0.003	0.050	0.269	0.418	0.235	0.025	6	(b)(d)(e)
Cu(II)	0	0	0.001	0.067	0.906	0.027		5	(b)(d)
Ag(I)	0	0.001	0.999					2	(b)(d)
Zn(II)	0	0	0.002	0.066	0.932			4	(a)
Cd(II)	0	0.013	0.159	0.438	0.372	0.018	0	6	(b)(d)(e)

A→	en					dien			
M	a_0	a_1	a_2	a_3	Ref.	a_0	a_1	a_2	N	References
Mn(II)	0.001	0.048	0.542	0.409	(a)	0	0.014	0.986	2	(c)(d)
Fe(II)	0	0	0.093	0.907	(a)	0	0.007	0.993	2	(c)(d)
Co(II)	0	0	0.008	0.992	(a)	0	0	1.000	2	(c)(d)
Co(III)										
Ni(II)	0	0	0	1.000	(b)(d)	0	0	1.000	2	(c)(d)
Cu(II)	0	0	0.990	0.0099	(b)(d)	0	1.000		1	(c)(d)
Ag(I)										
Zn(II)						0	1.000		1	(c)(d)
Cd(II)										

A→	trien				
M	a_0	a_1	a_2	N	Ref.
Mn(II)	0	0.014	0.986	2	(c)(d)
Fe(II)	0	0.002	0.998	2	(c)(d)
Co(II)	0	0.004	0.996	2	(c)(d)
Co(III)					
Ni(II)	0	0.00002	0.99998	2	(c)(d)
Cu(II)	0	1.000		1	(c)(d)
Ag(I)					
Zn(II)	0	1.000		1	(c)(d)
Cd(II)	0	0.006	0.994	2	(c)(d)

Table 23

Calculated Abundances for pA = 0

M \ A=NH_3	a_0	a_1	a_2	a_3	a_4	a_5	a_6	N	References
Co(II)	0	0	0.005	0.057	0.326	0.494	0.1184	6	(b)(d)(e)
Co(III)	0	0	0	0	0	0	1.000	6	(b)(d)
Ni(II)	0	0	0	0.005	0.079	0.442	0.474	6	(b)(d)(e)
Cu(II)	0	0	0	0.006	0.763	0.231		5	(b)(d)
Ag(I)	0	0.0001	0.9999					2	(b)(d)
Zn(II)	0	0	0	0.009	0.991			4	(b)(d)
Cd(II)	0	0	0.003	0.073	0.620	0.298	0.006	6	(b)(d)(e)

A →	en					dien				
M	a_0	a_1	a_2	a_3	Ref.	a_0	a_1	a_2	N	References
Mn(II)	0	0.001	0.117	0.882	(a)	0	0.001	0.999	2	(c)(d)
Fe(II)	0	0	0.010	0.990	(b)(d)	0	0.001	0.999	2	(c)(d)
Co(II)	0	0	0.001	0.999	(a)	0	0	1.000	2	(c)(d)
Co(III)										
Ni(II)	0	0	0	1.000	(b)(d)	0	0	1.000	2	(c)(d)
Cu(II)	0	0	0.910	0.091	(b)(d)	0	1.000		1	(c)(d)
Ag(I)										
Zn(II)						0	1.000			(c)(d)
Cd(II)										

A →	trien				
M	a_0	a_1	a_2	N	Ref.
Mn(II)	0	0.001	0.998	2	(c)(d)
Fe(II)	0	0	1.000	2	(c)(d)
Co(II)	0	0	1.000	2	(c)(d)
Co(III)					
Ni(II)	0	0	1.000	2	(c)(d)
Cu(II)	0	1.000		1	(c)(d)
Ag(I)					
Zn(II)	0	1.000		1	(c)(d)
Cd(II)	0	0.001	0.999	2	(c)(d)

Key to references in Tables 19, 20, 21, 22, 23.

a. Distribution of complex compounds from Bjerrum (9)

b. Complexity constants from Bjerrum (9)(10)

c. Complexity constants from Jonassen, Hurst, LeBlanc and Meibohm (24)

d. Distribution of complex compounds calculated for this paper.

e. Distribution of complex compounds calculated for this paper using p$\overline{[NH_3]}$ function agree substantially with those values calculated by Bjerrum (9) using pA$\overline{[NH_3]}$ function.

APPENDIX VII - Rest Effect Calculations

Table 24

Calculated Rest Effect in Selected Cu^{+2}-Amine Systems

Cu(II)-NH_3 System (log k_1=4.15; log k_2=3.50; log k_3=2.89; log k_4=2.13)

$R_{n,n+1}$ = log k_n − log k_{n+1} − $S_{n,n+1}$

$R_{1,2}$ = 4.15-3.50-.43 = 0.22
$R_{2,3}$ = 3.50-2.89-.35 = 0.26
$R_{3,4}$ = 2.89-2.13-.43 = 0.33

Cu(II)-en System (log k_1 = 10.55; log k_2 = 9.05)

$R_{1,2}$ = 10.55-9.05-.90 = +0.65

Cu(II)-pr System (log k_1 = 10.58; log k_2 = 9.08)

$R_{1,2}$ = 10.58-9.08-.90 = +0.60

Cu(II)-N,N'-di Me en System (log k_1 = 10.47; log k_2 = 7.63)

$R_{1,2}$ = 10.47-7.63-.90= 1.94

Cu(II)-N,N'-di Et en System (log k_1 = 9.30; log k_2 = 6.32)

$R_{1,2}$ = 9.30-6.32-.90= 2.08

Cu(II)-N,N'-di n-pr en System (log k_1 = 8.79; log k_2 = 5.55)

$R_{1,2}$ = 8.79-5.55-.90= 2.34

Cu(II)-N,N'-di Bu en System (log k_1 = 8.67; log k_2 = 4.84)

$R_{1,2}$ = 8.67-4.84-.90= 2.93

Table 25

Calculated Rest Effect in Selected Zn^{+2} Amine Systems

Zn-NH_3 System (log k_1 = 2.37; log k_2 = 2.44; log k_3 = 2.50; log k_4 = 2.15)

$R_{n,n+1}$ = log k_n - log k_{n+1} - $S_{n,n+1}$

$R_{1,2}$ = 2.37 - 2.44 - .43 = -0.50
$R_{2,3}$ = 2.44 - 2.50 - 0.35 = -0.41
$R_{3,4}$ = 2.50 - 2.15 - 0.43 = -0.08

Zn-py System (log k_1 = 1.42±0.3; log k_2 = -0.30±0.3; log k_3 = 0.49±0.7; log k_4 = 0.32±0.3)

$R_{1,2}$ = 1.42 + 0.30 - .43 = 1.29
$R_{2,3}$ = -0.30 - 0.49 - 0.35 = -1.14
$R_{3,4}$ = 0.49 - 0.32 - 0.43 = -0.26

Zn-en System (log k_1 = 5.71; log k_2 = 4.66; log k_3 = 1.72)

$R_{1,2}$ = 5.71 - 4.66 - 0.68 = 0.37
$R_{2,3}$ = 4.66 - 1.72 - 0.97 = 1.97

Zn-en System*

$R_{1,2}$ = 5.71 - 4.66 - .60 = 0.45
$R_{2,3}$ = 4.66 - 1.72 - .48 = 2.46

Zn-o-phen System (log k_1 = 6.43; log k_2 = 5.72; log k_3 = 4.85)

$R_{1,2}$ = 6.43 - 5.72 - 0.68 = 0.03
$R_{2,3}$ = 5.72 - 4.85 - 0.97 = -0.10

Zn-o-phen System*

$R_{1,2}$ = 6.43 - 5.72 - 0.60 = 0.11
$R_{2,3}$ = 5.72 - 4.85 - 0.41 = +.39

Zn-pr System (log k_1 = 5.89; log k_2 = 4.98; log k_3 = 1.70)

$R_{1,2}$ = 5.89 - 4.98 - 0.68 = 0.23
$R_{2,3}$ = 4.98 - 1.70 - 0.97 = 2.31

Zn-pr System*

$R_{1,2}$ = 5.89 - 4.98 - 0.60 = 0.31
$R_{2,3}$ = 4.98 - 1.70 - 0.48 = 2.80

---

* Calculated on assumption first molecule chelates whereas second and third are bound through only one amine group.

Table 26

Calculated Rest Effect in Selected Cd^{+2} Amine Systems

Cd-NH_3 System (log k1 = 2.65; log k2 = 2.10; log k3 = 1.44; log k4 = 0.93)

$R_{n,n+1}$ = log k_n - log k_{n+1} - $S_{n,n+1}$

$R_{1,2}$ = 2.65-2.10-0.43 = 0.12
$R_{2,3}$ = 2.10-1.44-0.35 = 0.31
$R_{3,4}$ = 1.44-0.93-0.43 = 0.08

Cd-NH_2CH_3 System (log k1 = 2.745; log k2 = 2.06; log k3 = 1.13; log k4 = 0.61)

$R_{1,2}$ = 2.745-2.06-0.43 = 0.25
$R_{2,3}$ = 2.06-1.13-0.35 = 0.58
$R_{3,4}$ = 1.13-0.61-0.43 = 0.09

Cd-en System (log k_1=5.84; log k_2= 4.78; log k_3=2.07)

$R_{1,2}$ = 5.84-4.78-0.68 = +0.38
$R_{2,3}$ = 4.78-2.07-0.97 = +1.74

Cd-en System*

$R_{1,2}$ = 5.84-4.78-0.60 = 0.46
$R_{2,3}$ = 4.78-2.07-0.48 = 2.23

Cd-pr System (log k_1=5.42; log k_2= 4.55; log k_3=2.15)

$R_{1,2}$ = 5.42-4.55-0.68 = +0.19
$R_{2,3}$ = 4.55-2.15-0.97 = 1.43

Cd-pr System*

$R_{1,2}$ = 5.42-4.55-0.60= 0.27
$R_{2,3}$ = 4.55-2.15-0.48= 1.92

---

* Calculated on assumption first molecule chelates whereas second and third molecules are bound through only one amine group.

Table 27

Calculated Rest Effect in Selected Fe^{+2} Amine Systems

Fe-en System ($\log k_1 = 4.28$; $\log k_2 = 3.25$; $\log k_3 = 1.99$)

$R_{1,2} = 4.28-3.25-0.68 = 0.35$
$R_{2,3} = 3.25-1.99-0.97 = 0.29$

Fe-dipy System ($\log k_1 = 4.20$; $\log k_2 < 5.0$; $\log k_3 > 7.3$)*

$R_{1,2} = 4.20-5.0-0.68 = -1.48$
$R_{2,3} = 5.0-7.8-0.97 = -3.77$

Fe-o-phen System ($\log k_1 = 5.88$; $\log k_2 = ?$; $\log K_3 = 21.3$)*

$R_{1,2} = 5.88-6.9-0.68 = -1.70$
$R_{2,3} = 6.9-8.5-0.97 = -2.57$

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*See discussion following Table 10, Section III.

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